

Supplementary Material

Parametric Study and Multi-Objective Optimization of Fixed-Bed Fischer–Tropsch Reactor: The Improvement of FT Synthesis Products Formation and Synthetic Conversion

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1. Mathematical Modelling of a Fixed-Bed Reactor for Fischer–Tropsch Synthesis Process

A numerical analysis and mathematical modelling can be used as an effective tool to provide knowledge about a catalytic reaction. Experimental studies are typically very expensive; whereas theoretical modelling studies require only a suitable model formulation and adequate physicochemical data. The information such as temperature, reactant composition and products' distributions obtained from the modelling is significantly helpful in reactor design, scale-up, the understanding of its behaviour in operation and predicting the effect of changing operating conditions. Here, the procedures in developing the mathematical model of a fixed-bed FT synthesis reactor that is used in the evaluation of the kinetic parameters, parametric studies and optimization of the reactor operations, are discussed in detail. In addition, the general selection criteria and the governing equations used in the modelling of a fixed-bed reactor are explained. In principle, a model should be tailored for its main purpose. It should be as simple as possible, but still include a sufficient representation of the essential mechanisms involved. Hence, several assumptions were taken into account in order to facilitate the computational procedure and the model equations; such as species balance, continuity equation and pressure drop. An algorithm was developed to solve the system of equations which includes the mathematical description of the reactor model, reaction kinetics, and steps towards estimating kinetic parameters.

In general, procedures for obtaining the kinetics parameters involved several steps; such as (i) selection and construction of experimental equipment; (ii) planning of experiments; (iii) conducting them; (iv) checking the consistency of the experimental data; (v) developing kinetics models; (vi) developing a mathematical model of a catalytic reactor by derivation of governing conservation equations; and (vii) evaluation of the kinetics parameters. The latter tasks can be carried out by classical methods, which are mostly on the basis of graphical procedures; or by modern approaches, which rely on statistical methods as will be explained in section 3.2. The evaluation of kinetics parameters based on statistical methods necessitates the implementation of a particular kinetics model on a computer and subsequent parameter estimation; then, the physical and statistical consistency of the kinetics parameters has to be evaluated. If the values of the parameters are for some reason unacceptable, then the estimation of the parameters should be repeated, sometimes with additional experiments or by reducing the number of system parameters by simplifying the reactor model and/or kinetics model. Corresponding to the

procedures mentioned above, one can say that the following steps are the next sequences for the whole theoretical investigation of the model: (viii) validation of the mathematical model using the evaluated kinetics parameters in the latter task; (ix) parametric studies of effective independent variables to investigate the performance of the fixed-bed FT synthesis reactor over a Co/SiO₂ catalyst for conversion and selectivities; (x) numerical optimization of the operating conditions to maximize the FT synthesis conversion, selectivities and productions of favourable compositions. A block diagram of the complete process is illustrated in Figure S1.

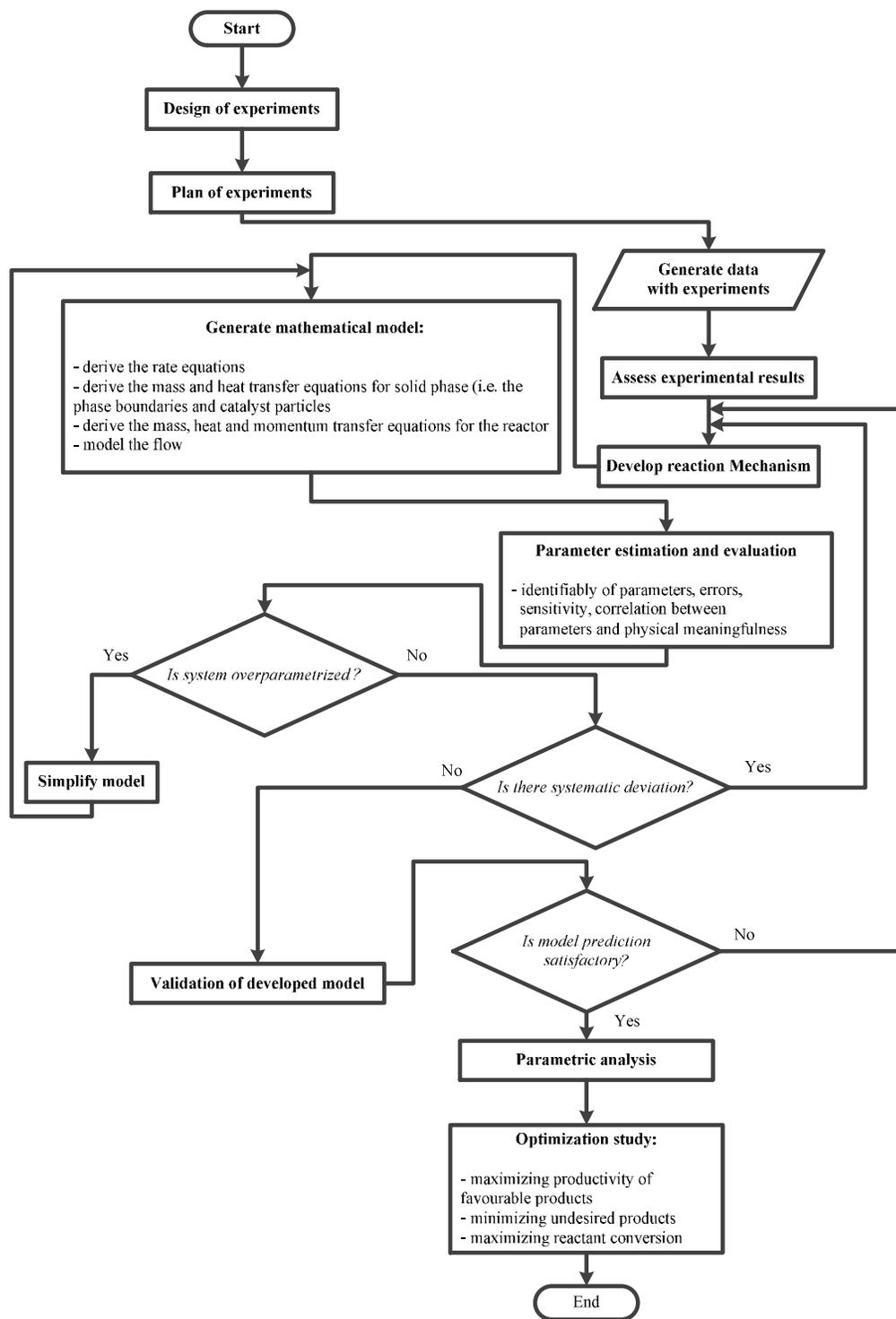


Figure S1 The whole process involved in the development of kinetics modelling of the FT synthesis process.

In a one-dimensional model (also known as a plug flow model), fluid properties (e.g. temperature, concentration and velocity) are assumed to be uniform over the tube cross-section. Hence, the gradients of these properties (i.e. the resistance to heat and mass transfer) in the radial and angular directions are neglected; the properties are varied only in the axial direction (e.g. along the reactor bed length).

2. Algorithm Development and Numerical Method

Regardless of the technique (e.g. finite difference or finite element method) that is used to solve the system of differential equations (e.g. ODE or PDE), it is necessary to build the solution method into an algorithm which will be turned into a computer program. The intention was to provide recipes for solving the final problem in which experimental data is predicted satisfactorily by a mathematical model. Here, the developed algorithm was found useful in solving the reactor problem not only in a fixed-bed reactor but also in a different reactor type. A solution algorithm was presented that is effective in solving the single tube reactor model. Such a solution methodology can be applied to a wide variety of problems which require the solution of sets of coupled non-linear partial differential equations (e.g. 2nd order differential equations ¹). The algorithm was applied after the decision was made about which numerical scheme to employ and the equations were reformulated in the appropriate manner. The algorithm illustrated in Figure S2 and Figure S3 referred to a steady-state one-dimensional model; however, the methodology is easily extended to two- or three-dimensional models or shifted to an unsteady-state condition.

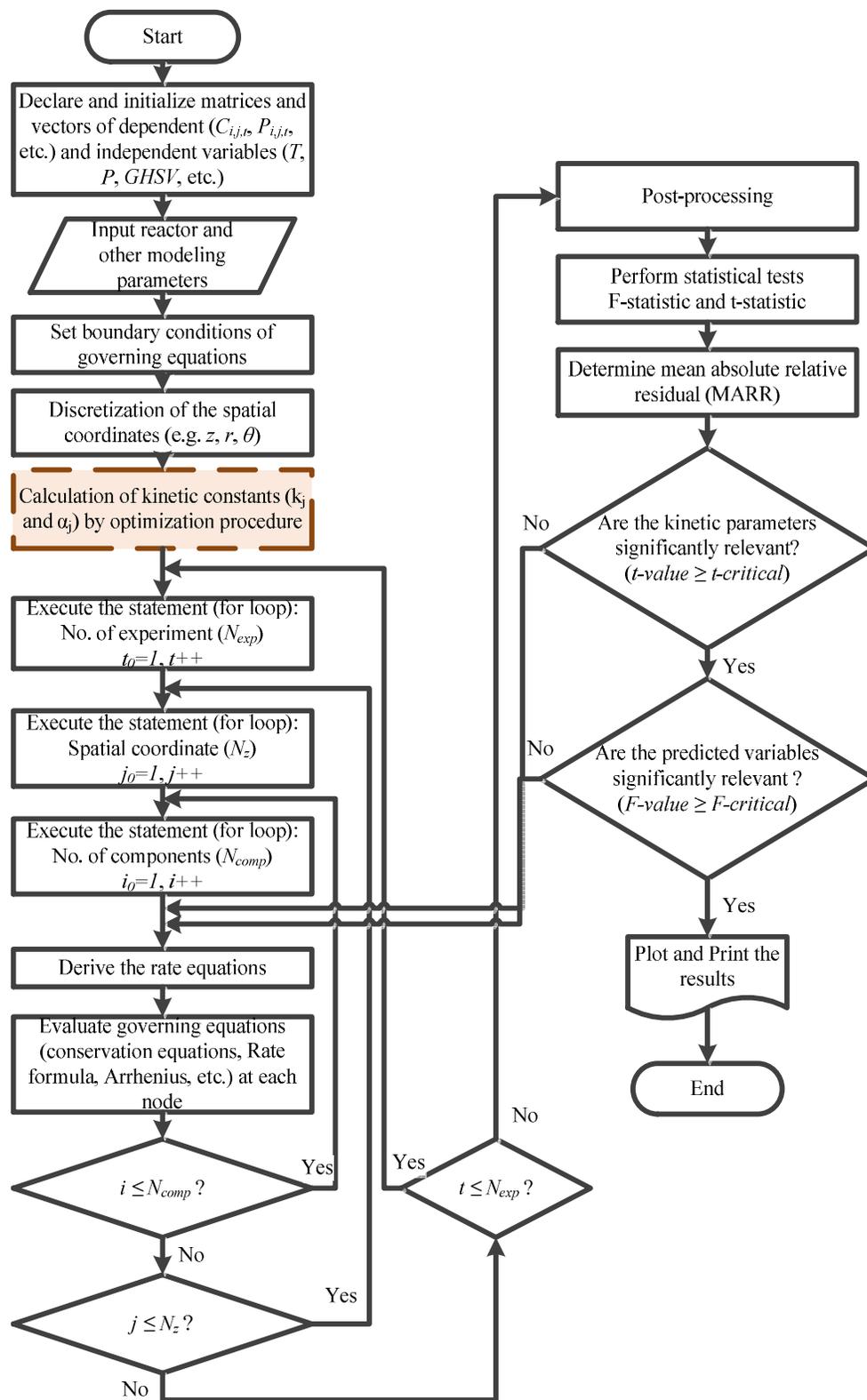


Figure S2 Flow-chart diagram of mathematical and kinetics modelling procedure.

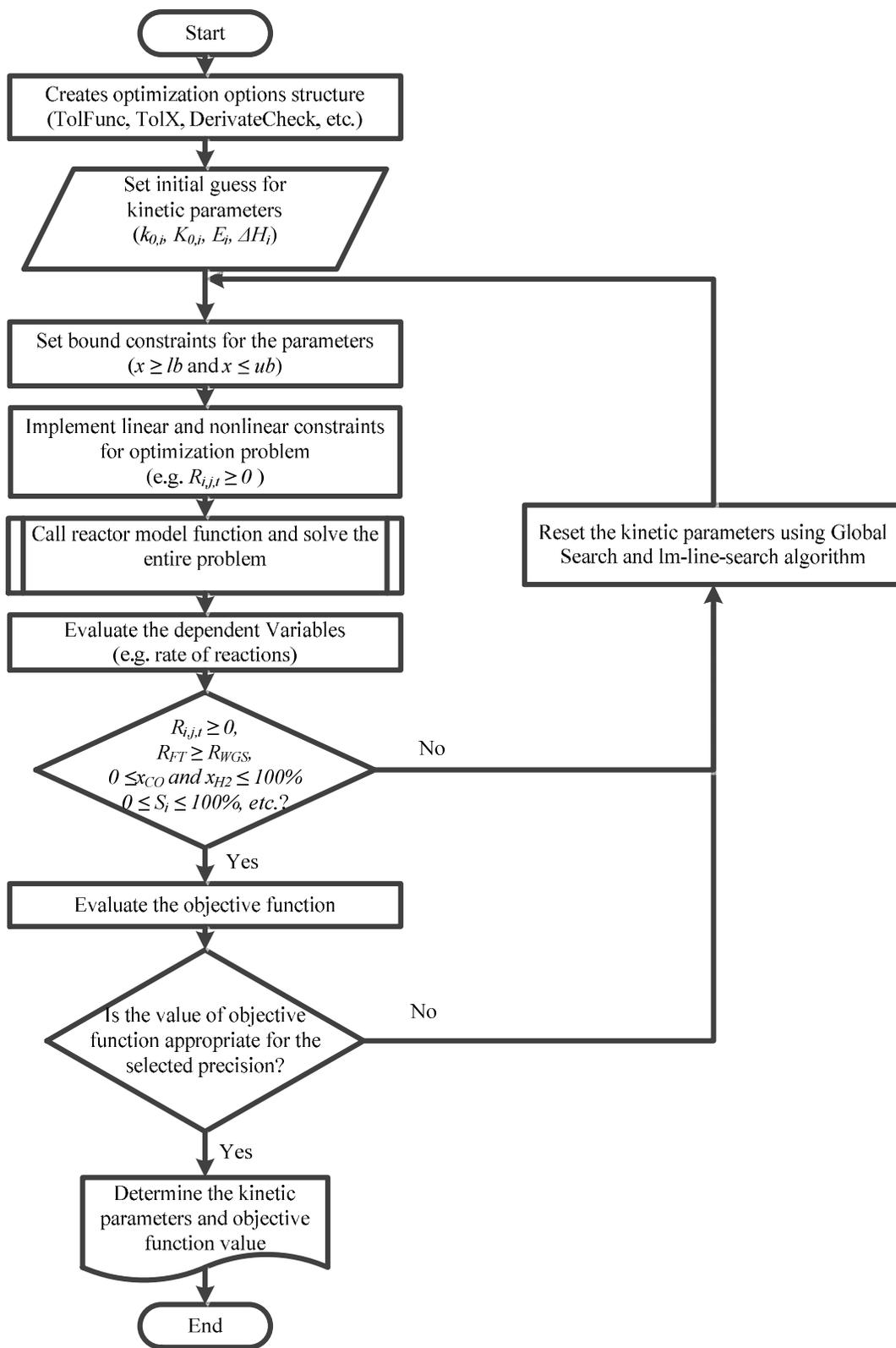


Figure S3 Flowchart diagram of optimization procedure in estimation of kinetics parameters.

The mole balance equation is, in fact, the most difficult to solve because it is highly nonlinear due to the nature and order of reaction rates in terms of concentration of different species such as CO, CO₂, H₂ and H₂O. The unknown dependent variables in the reactor were the concentration, mole fraction and partial pressure of the species in the flow direction; the rate equation for the multiple reactions; as well as the fluid velocity and total pressure of the system. The approach was to solve each differential equation in turn, cycling through the equations one after another, repeating the process until a final converged solution was gained at the reactor outlet. It was assumed that the domain was discretized and that the solution was calculated at a number of fixed points (locations) along the length of the packed bed. The steps were as follows:

- i.* The physical and chemical parameters involved in the reactor model were initialized. These parameters were either fixed values or functions of temperature, concentration, pressure and/or velocity. Some of these values were stored in a data file and some others were built into library of functions to be called by the main MATLAB program.
- ii.* The temperature was assumed to be constant. Therefore, the species partial pressure, concentration, and mole fraction, as well as the total pressure and velocity of the fluid flow were initialized.
- iii.* The total pressure of the fluid flow i.e. Equation 6, was solved using the most recent values for concentration and partial pressure. The value of the pressure was then updated to be used to solve the density of the fluid mixture i.e. Equation 4.
- iv.* The fluid velocity field i.e. Equation 3, was then determined by using the updated (the most recent) value of pressure and fluid velocity which was stored as an input to the next steps.
- v.* Then, the last stored data were used to calculate the partial pressure (Equation 2), concentration (Equation 1), mole fraction and weight fraction of each chemical compound defined in the reactor problem.
- vi.* Steps (*ii*) to (*v*) were repeated using several nested loops until all the unknown dependent variables were solved at each specified fixed node (location) in the spatial coordinate and for different experimental cases (conditions).
- vii.* The results were then stored in the library and data file to be used in the post processing section that was used to perform statistical analysis, such as *F*-test and *t*-test to ensure that the model and the parameters were statistically significant. Also, the relative residual between the calculated and measured data was determined to check the accuracy of the prediction.
- viii.* A statement was made so that if the accuracy of the prediction and/or statistical analysis failed, then the model must be rejected and steps (*iii*) to (*vii*) must be repeated.
- ix.* Finally, the results were printed and plotted for further analysis and investigation.

$$u_s \frac{\partial C_i}{\partial z} = \alpha^* \beta \sum_{j=1}^{NR} v_{ij} R_j - C_i \frac{\partial u_s}{\partial z} \quad \text{Equation 1}$$

$$\frac{u_s}{R_g T} \frac{\partial p_i}{\partial z} = \alpha^* \beta \sum_{j=1}^{NR} v_{ij} R_j - \left(\frac{P_T}{R_g T} \frac{\partial u_s}{\partial z} \right) \quad \text{Equation 2}$$

$$\rho_f \frac{\partial u_s}{\partial z} = -u_s \frac{\partial \rho_f}{\partial z} \quad \text{Equation 3}$$

$$\frac{\partial \rho_f}{\partial z} = \frac{\partial \left(\frac{P_T M_m}{R_g T} \right)}{\partial z} = \frac{M_m}{R_g T} \frac{\partial P_T}{\partial z} - \frac{M_m P_T}{T^2 R_g} \frac{\partial T}{\partial z} \quad \text{Equation 4}$$

$$M_m = \sum_{i=1}^{NS} Y_i M_i \quad \text{Equation 5}$$

$$\frac{dP_T}{L} = \frac{150 G \mu_m (1 - \varepsilon)^2}{d_p^2 \rho_f \varepsilon^3} + 1.75 \frac{G^2 (1 - \varepsilon)}{\rho_f d_p \varepsilon^3} \quad \text{Equation 6}$$

In order to solve the dependent variables (e.g. concentrations, partial pressures, reactants' conversions and products' selectivity) a numerical method was used. Euler's and finite difference approximation were employed to solve Equation 1 to Equation 5 at each point ($z_1, z_2, z_3, \dots, z_{n-1}$, and z_n) from an initial value of z_0 . The backward finite difference for the first order ODEs was programmed in the space increments. Therefore, the node z_n is directly calculated from the z_{n-1} by computing the derivative at z_n . The exact solution was converged by reducing the step size which leads to a decrease of the error. The variables were calculated along the axial dimension in multi-nested loops. The advantage of this combined method was that the percentage error produced by the program code was negligible.

The model was discretized in the dimension needed by the code (i.e. "z", "i" and "t" which are length, number of species and number of experimental conditions, respectively) as follows:

$$\begin{aligned} \text{Size of the mesh} &= [\text{Number of nodes in z direction}] \times \\ &[\text{Number of species}] \times [\text{Number of experimental conditions}] \end{aligned} \quad \text{Equation 7}$$

3. Optimization Methodology for Kinetics Parameter Estimation

3.1. Optimization Method

Parameter estimation problems were stated as minimizing the objective function that measured the correctness of the fit of individual models with respect to a given experimental data set. Each presented model contained a number of unknown independent parameters so that the values should be estimated by an advanced optimization technique to obtain a model fitting the experimental results. The procedures were as follows: the value of the dependent variables (i.e. reaction rates, conversion and selectivity of different components) were predicted by the model; a function ' f ', contained independent variables (i.e. temperature (T), pressure (P_T) and gas hourly space velocity (GHSV)) and parameters (i.e. kinetics parameters such as kinetic rate constants (k_i), adsorption equilibrium constants (K_i) and activation energies (E_j)). The choice of optimization technique depends on the level of sophistication of the problem. In the case of a reactor problem, the reactor model along with the

chemical reaction networks was stated as a nonlinear programming (NLP) problem, especially when a high order of reaction rates builds the network. There is evidence that traditional (gradient-based), local, optimization methods fail to arrive at satisfactory solutions and are not suitable for nonlinear problems. As a consequence, the values of the parameters were estimated by an advanced global optimization technique, which is a powerful and objective tool for this purpose. Among different global optimization methods, the Global Search algorithm together with the Levenberg-Marquardt (LM) algorithm were delivered as an alternative to surmount the difficulties mentioned above. This method is capable of avoiding convergence to the local minima (sub-optimal solutions) during the search process. In the optimization procedure, the independent parameters (e.g. kinetics parameters) were subject to upper and lower bounds acting as inequality constraints ($p_{LB} \leq p \leq p_{UB}$). The optimization problem aimed at estimating the kinetics parameters in such a way that the objective function was not just minimized, but also the global minimum value of the objective function was achieved. The problem consisted of $N_{exp} \times (N_{resp} + N_v + N_p)$ Partial Differential Equations (PDEs) that described the changes of concentration of reactants and products, as well as fluid velocity and density along the reactor bed length and one Ordinary Differential Equation (ODE) for that of total pressure (P_T). The term N_{exp} denotes the total number of experimental runs; N_{resp} is the number of responses (i.e. chemical species); N_v is the equation related to the velocity field and N_p is related to that of fluid density. The goal was to find such numerical values of the parameters that the model gives the best possible agreement with the experimental data. From the governing balance equations in the model, it is clear that the model was non-linear with respect to the parameters and variables. For estimation of the kinetic models, the dependent variable (i.e. model responses in the regression procedure) were the outlet conversion of CO, the selectivities of CO₂, CH₄, C₂H₄, C₂H₆, C₃H₆, C₃H₈, C₄H₁₀, C₅H₁₂, C₆H₁₂, C₇H₁₆ and overall selectivity of C₅₊ that represents the overall formation of liquid products. The objective function is defined by Equation 8.

$$f_{j,obj} = \left(\frac{y_j^{exp} - y_j^{cal}}{y_j^{exp}} \right)^2 \quad j = 1, 2, 3, \dots, N_{exp} \quad \text{Equation 8}$$

Where y_j^{exp} and y_j^{cal} are the measured and predicted values of conversions of reactants or the selectivities of products, respectively. Due to the complexity of the models, a multi-response objective function was introduced, in the following form:

$$OF = \sum_{i=1}^{N_{resp}} \sum_{j=1}^{N_{exp}} \left(w_{i,j} \left(\frac{y_{i,j}^{exp} - f(x_{i,j}, p)}{y_{i,j}^{exp}} \right)^2 \right) \quad \text{Equation 9}$$

Where 'i' denotes each component in the reaction mixture; $w_{i,j}$ represents the weighting factor of the response 'i' in experimental run 'j', which was used as the experimental scattering varying between different data. Those responses with the most accurate measurement and/or with special significance in the regression were provided with greater weights. In fact, the weighting factor expressed the relative importance of the response 'i' in experimental run 'j'; $f(x_{i,j}, p)$ is the value of model prediction.

3.2. Data Analysis

As explained in section 3.1, to avoid getting trapped in local minima, the globally kinetic parameters of the various rival models were estimated using the combined GlobalSearch algorithm and Levenberg-Marquardt (LM) algorithm. Then, the statistical tests as well as physicochemical constraints were employed to evaluate the significance of the models and kinetic parameters. The optimisation procedure was designed to find the optimal minimum value of the objective function defined in section 3.1, which delivered: (i) a reasonable fit to the measured values; (ii) physically meaningful values of the kinetic model parameters; (iii) acceptable values of statistical parameters, e.g. F_{value} for the predicted model as well as t_{value} for the estimated kinetic parameters and these criteria were studied in the following sections (3.3-3.6).

3.3. Physicochemical Constraints

For scanning the models by parameter optimization, several physicochemical criteria were applied, such as those defined for rate constants (k_j), adsorption equilibrium constants (K_i) and activation energies (E_j). Kinetic rate constants and adsorption equilibrium constants should be positive. Also, the values of activation energies should be positive and for different components e.g. methane, ethane, WGS, higher paraffin and olefins' formation should be in the range of values reported in the previous work ².

3.4. Mean Absolute Percentage Deviation (MAPD)

Equation 10 indicates the relative residual (RR) percentage error between predicted values and experimental data of individual response 'i'. This equation was used to indicate the deviation between the model and experiment for each individual response. The RR (%) values for the responses of each model were presented in the previous work ².

$$RR_i(\%) = \frac{m_i^{exp} - m_i^{cal}}{m_i^{exp}} \times 100 \quad \text{Equation 10}$$

In order to measure the accuracy of the fit of the models relative to the experimental data, the results were analysed quantitatively by the mean absolute percentage deviation (MAPD) using Equation 11. The MAPD (%) values were determined for developed mechanistic models as well as for power-law rate expression ² and compared with those from literature models.

$$MAPD(\%) = \frac{1}{N_{exp}N_{resp}} \sum_{i=1}^{N_{resp}} \left[\sum_{j=1}^{N_{exp}} \left(\left| \frac{y_{i,j}^{exp} - f(x_{i,j}, p)}{y_{i,j}^{exp}} \right| \times 100 \right) \right] \quad \text{Equation 11}$$

3.5. F-test Analysis

In addition to providing an excellent fit to the experiments, all the models should be significantly relevant and physically meaningful. One way to assure the significance of the predicted model results is the statistical

analysis called the F -test, where the significances of the overall regression were statistically determined. The F -test was used to see if the fit has any significance at all. The test was performed by taking two factors into account:

- I. SST term that is the total sum of squared deviations of the experimental data with respect to their mean value.
- II. SSE term that is the residual sum of squared deviations of the experimental results with respect to the predicted values by the model.

Finally, the F_{ratio} for each individual response and the total responses were calculated by Equation 12. The F_{ratio} determined for the models were given in ².

$$F_{ratio} = \frac{(SST - SSE) / (m - 1)}{SSE / (n - m)} = \frac{(\sum_{j=1}^{N_{exp}} (y_{j,exp} - \bar{y})^2 - \sum_{j=1}^{N_{exp}} (y_{j,exp} - y_{j,pred})^2) / (m - 1)}{\sum_{j=1}^{N_{exp}} (y_{j,exp} - y_{j,pred})^2 / (n - m)} \quad \text{Equation 12}$$

In this equation, n is a degree of freedom of a number of data points ($N_{exp} \times N_{resp}$) and m is corresponding to the number of kinetics parameters. It is possible to reject the null hypothesis and hence accept the model. This happens when the F_{ratio} determined for the responses are higher than the value of $F_{critical}$ which is the corresponding tabulated value ³⁻⁵ ($F_{ratio} > F_{critical}(m - 1, n - m; 1 - \alpha)$); $F_{critical}$ is the tabulated α -percentage point of the F -distribution with $m - 1$ and $n - m$ degrees of freedom. If the calculated value is larger than the tabulated value (can be found in ²), there is a probability of $1 - \alpha$ (e.g., 99%) that the model is adequate and the regression is considered to be meaningful, therefore the model is accepted. Among a set of rival models, the one with the highest F_{ratio} would be considered the ‘‘best’’ and that it would be statistically adequate.

3.6. t -test Analysis

The t -test was performed to ensure that the kinetics parameters obtained by the optimization, were significantly relevant. The estimated kinetics parameters were tested for their significance based on their individual t_{value} calculated by the procedure below (see Table S1). The parameter with the lowest t_{value} is the least significant parameter and here a parameter is evaluated as insignificant if its t_{value} is less than the $t_{critical}$ from the tabulated values that can be obtained from the literature ^{3, 4, 6}. For the optimum kinetics model, the calculated t_{value} of the kinetic parameters was determined for the models and presented in ². The steps for calculating the t_{value} of the kinetic parameters are as follows:

- I. Determination of the hypothesized or population mean (μ). When the errors are normally distributed with zero mean and constant variance, the random variables are distributed like the normal (Gaussian) distribution. At the given probability level (e.g. 99%), the calculated n values have to exceed tabulated t_{value} for the parameter to be significantly different from a reference value, which is zero ($\mu=0$). This

property is used in a two-sided t -test to verify if the estimated parameters differ from a reference value (zero), when other parameters are kept constant at their optimal estimated value.

- II. Computation of the sample mean (\bar{X}) (see Equation 13).
- III. Computation of the sum of the squares of the individual parameters obtained from each experimental run (see Equation 14).
- IV. Computation of the sum of the square difference as expressed (see Equation 15).
- V. Computation of the estimated variance of the sample data (see Equation 16).
- VI. Computation of the standard error of the mean (SEM) (see Equation 17).
- VII. Calculation of the t_{value} from (see Equation 18).
- VIII. Computation of the degree of freedom (see Equation 19).
- IX. Computation of the critical value for t (called t_{score} or $t_{critical}$) with that degree of freedom and probability value using a provided table in the literature^{3,4,6}.
- X. Comparison of the calculated t_{value} of individual kinetic parameters to the tabulated $t_{critical}$ (can be found in²).

When $t_{value} > t_{critical}(n - m; 1 - \alpha)$ the hypothesis that the parameter would be zero can be rejected. The quantity $t_{critical}(n - m; 1 - \alpha)$ is the tabulated α percentage point of the t -distribution with $n - m$ degrees of freedom. There are limits on the complete collection of reference values which are not significantly different from the optimal estimates, a_j at the selected probability level $1 - \alpha$, provided that the other estimates are kept constant upon their optimal estimate. They are symmetrical with respect to the optimal point estimate a_j . Hence, the confidence intervals of individual kinetic parameters a_j are defined by: $a_j - CF < a_j < a_j + CF$.

Table S1 Steps through the computation of t_{value} to test the level of significance of obtained kinetic parameters

Step (II)	Step (III)	Step (IV)	
Equation 13	Equation 14	Equation 15	
$\bar{X} = \frac{\sum_{j=1}^{N_{exp}} X}{n}$	$\sum_{j=1}^{N_{exp}} X^2$	$SS = \sum_{j=1}^{N_{exp}} X^2 - \frac{\left(\sum_{j=1}^{N_{exp}} X\right)^2}{n}$	
Step (V)	Step (VI)	Step (VII)	Step (VIII)
Equation 16	Equation 17	Equation 18	Equation 19

$$s^2 = \frac{SS}{n - 1}$$

$$SEM = \sqrt{s^2/n}$$

$$t_{value} = \frac{\bar{X}}{SEM}$$

$$df = n - 1$$

4. References

1. Moazami, N.; Wyszynski, M.; Mahmoudi, H., Modeling of catalytic monolith reactor for reforming of hexadecane with exhaust gas. *International Journal of Hydrogen Energy* **2013**, *38* (27), 11826-11839.
2. Moazami, N.; Wyszynski, M. L.; Tsolakis, A.; Rahbar, K.; Mahmoudi, H., A comprehensive study of kinetics mechanism of Fischer-Tropsch synthesis over cobalt-based catalyst. *Chemical Engineering Science* **2017**.
3. Himmelblau, D. M., *Process analysis by statistical methods [by] David M. Himmelblau*. Wiley: New York, 1970.
4. Berendsen, H. J., *A student's guide to data and error analysis*. Cambridge University Press: 2011.
5. Trek, S. F Distribution Calculator: Online Statistical Table. <http://stattrek.com/online-calculator/f-distribution.aspx>.
6. Trek, S. T Distribution Calculator: Online Statistical Table. <http://stattrek.com/online-calculator/t-distribution.aspx>.